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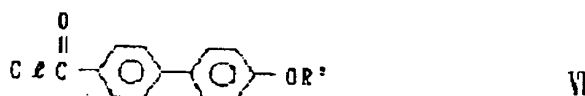
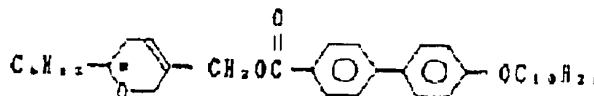
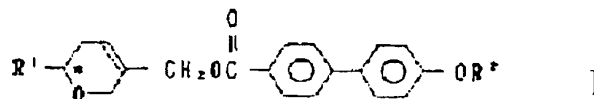
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TITLE : OPTICALLY ACTIVE COMPOUND AND
LIQUID CRYSTAL COMPOSITION
CONTAINING THE SAME



ABSTRACT : NEW MATERIAL: A compound of formula I (R^1 is 1-18C alkyl; R^2 is 2-24C alkyl; *is asymmetric).

EXAMPLE: 3-(6-Hexyl-5,6-dihydro-2H-pyranyl)methyl 4-(4-decyloxyphenyl)-benzoate of formula II.

USE: Useful as an electrooptical element after blended with a liquid crystal compound. The compound of formula I forms liquid crystals responsible in a low, wide temperature range and having excellent high fast responsibility.

PREPARATION: A compound of formula III is reacted with a compound of formula: $\text{CH}_2=\text{CHCN}$ and the reaction product is reacted with MeOH/HCl . The reaction product of formula IV is treated with CrO_3 and with NaOH , and subsequently reacted with LiAlH_4 to provide a compound of formula V, which is reacted with a compound of formula VI in the presence of triethylenediamine and NaH .

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(54) Title of the Invention: Optically-Active Compounds and Liquid Crystal Compositions Containing Them

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Specification

1. Title of the Invention: Optically-Active Compounds and Liquid Crystal Compositions Containing Them

2. Scope of Patent Claims

(1) The optically-active chemical compound represented by General Formula (I)

/formula/

(In the formula, R¹ is an alkyl group with a carbon number of 1 - 18, R² is an alkyl group with a carbon number between 2 and 24 and the asterisk (*) indicates asymmetry.)

(2) The liquid crystal composition containing at least one type of optically-active chemical compound represented by the General Formula (I).

/formula/

(In the formula, R¹ is an alkyl group with a carbon number of 1 - 18, R² is an alkyl group with a carbon number between 2 and 24 and the asterisk (*) indicates asymmetry.)

(3) The liquid crystal composition described in Claim 2 of the Scope of Patent Claims containing at least one chemical compound expressed by the General Formula (II) (where R3 and R4 indicate alkyl groups with carbon numbers between 1 and 24), and containing at least one of the optically-active chemical compounds shown in the General Formula (I) above.

/formula/ (II)

(4) The liquid crystal composition described in Claim 2 of the Scope of Patent Claims that contains at least one type of chemical compound expressed using the General Formula (III), (where R5 and R6 are alkyl groups or alkenyl groups with carbon numbers between 1 and 24) and that contains at least 1 type of optically-active chemical compound expressed by the General Formula (I) above.

/formula/ (III)

3. Detailed Description of the Invention

Industrial Fields of the Invention

This invention pertains to new, optically-active chemical compounds. The chemical compounds of this invention are blended with other liquid crystal chemical compounds and used as electric optical elements.

Prior Art

At present, liquid crystal elements are being widely used as display elements of all sorts because of their low-voltage drive characteristics, their low electric power consumption, their compact size, their thin shape and other features.

Nearly all of the display elements that are used in practical applications at this point are the TN (Twisted Nematic) type that use nematic liquid crystals. One shortcoming, however, is that this display format has a response speed that is on the order of several msec at best. More recently it has been learned that faster response times are possible using ferroelectric smectic liquid crystals.

A typical example of a ferroelectric smectic liquid crystal is the 4 - (4 - n - decyl oxybenzylidene amino) - 2 - methyl butyl ester cinnamate (hereafter abbreviated to "DOBAMBC.") silica chemical compounds that were developed in 1975 by R. B. Meyer et al. It exhibits ferroelectric characteristics in its chiral smectic C phase. (Journal Physique (J. Physique), 36, L - 69 (1975)).

Recently, when response speed characteristics on a μ sec order were discovered in DOBAMBC thin film (according to N. A. Clark et al (Applied Physics Letters (Appl. Phys. Lett.), 36, 899 (1980)), it has been getting attention as a material that can be used in not only liquid crystal televisions and other displays, but also in optical printer heads, optical fourier transformation elements, light bulbs and other elements related to optoelectronics.

Be that as it may, however, it is not easy to prepare known ferroelectric liquid crystals that have a simple composition for use in practical applications with a broad temperature range. There is a method that increases the temperature range of chiral smectic C phase by blending several types of materials, but at present these have not reached the point of practical applications. This is due to insufficient types of ferroelectric crystals and materials for mixing.

The following chemical compounds have been reported (Tetsuya IKEMOTO et al, Collected Papers of the 15th Conference on Liquid Crystals, 1 A 05 (1989)) as containing six-member ring, cyclic asymmetry.

/formula/

| R | Y | Z |
|-------------------------------------|-----|---|
| C ₆ H ₁₃ O | - | H |
| C ₇ H ₁₅ O | - | H |
| C ₈ H ₁₇ O | - | H |
| C ₁₀ H ₂₁ O | - | H |
| C ₁₂ H ₂₅ O | - | H |
| C ₁₆ H ₃₃ O | - | H |
| C ₈ H ₁₇ O | OOC | H |
| C ₈ H ₁₇ O | COO | H |
| C ₈ H ₁₇ O | COO | C |
| C ₁₀ H ₂₁ COO | OCH | H |
| C ₁₃ H ₂₇ COO | OCH | H |

Note, however, that the temperature range of the chiral smectic phase of these compounds is high and not practical.

Problems The Invention Attempts To Solve

This invention solves the problems described above that are associated with DOBAMBC as well as with a number of chemical compounds that have been proposed subsequently. It provides a compound that has superior physicochemical stability and can be mixed with other chemical compounds to give it a lower and broader temperature range.

Means for Solving The Problems

This invention provides a liquid crystal composition that contains at least one type of mixed component in addition to the optically-active chemical composition represented by the General Formula (I).

/formula/ (I)

(In the formula, R¹ is an alkyl group with a carbon number of 1 to 18, R² is an alkyl group with a carbon number of 2 to 24, an asterisk "*" indicates asymmetry.)

Unlike DOBAMBC, for example, the chemical compounds of this invention do not have a Schiff base so they are physicochemically stable. Other characteristics include the fact that they become ferroelectric liquid crystals when mixed with other chemical compounds. This gives them a temperature range that is low and broad with a superior response time.

In the General formula (I) above, R¹ alkyl groups with carbon numbers from 1 through 18 include methyl groups, ethyl groups, propyl groups, hexyl groups, decyl groups, dodecyl groups, hexadecyl groups, octadecyl groups and other straight-chain or branched-chain alkyl groups. Of these, the hexyl groups are preferred. R² alkyl groups with carbon numbers from 2 to 24 include ethyl groups, propyl groups, hexyl groups, decyl groups, dodecyl groups, octadecyl groups, docosyl groups, tetracosyl groups and other straight-chain or branched chain alkyl groups. Of these, the decyl groups are preferred.

It is preferred that the optically-active chemical compounds represented by the General formula (I) be synthesized from the optically-active beta-hydroxyl alkanonitrile that is obtained using known methods (Hiroyuki NOHIRA et al, Papers of the 54th Spring Conference of the Japan Chemical Society 3 III O06 (1987), Hiroyuki NOHIRA et al, Articles of the Saitama, University Engineering Department No. 20, 33 (1986)) with the synthesis route shown below.

/formula/
CrO₃, pyridine

/formula/
Triethylene Diamine, NaH

/formula/ (I)

Note: R¹, R² and the asterisk "*" in the synthesis route above are the same as for Formula (I).

Additionally, the liquid crystal compositions of this invention contain at least one type of mixture of optically-active chemical compounds represented by the General formula (I). For example, if these optically-active chemical compounds are mixed with the chemical compounds in the known General Formulae (II) or (III) shown below, they can be turned into ferroelectric liquid crystals with a low, broad range of temperatures.

It is preferred that the liquid crystal composition produced have a ratio of 0.1 to 99 of wt %, especially, 1 to 90 wt % in the case of the optically-active chemical compounds of this invention shown in the General formula (I).

Chemical Compound Represented by the General Formula (II) (In the formula, R³ and R⁴ represent alkyl groups with carbon numbers from 1 to 24.) (See JSP S56-53661.)

/formula/ (II)

Chemical Compound Represented by the General Formula (III). (In the formula, R⁵ and R⁶ represent alkyl groups or alkenyl groups with carbon numbers from 1 to 24.) (See H. Zschke, Journal für praktische Chemie, 317, 617 (1975).)

/formula/ (III)

Of the elements in the chemical compound shown in the General Formula (II), it is preferred that R³ be an octyl group, and R⁴ be a nonyl group. Of the elements in the chemical compound shown in the General Formula (III), it is preferred that R⁵ be a nonyl group, and R⁶ be a nonenyl group.

Effect of the Invention

The compound of this invention is physicochemically stable and will make compositions containing ferroelectric with a low, broad temperature range. It is well-suited to use in electrooptical elements.

Embodiments

We will describe this invention more specifically using the embodiments below. Note that the measurement of the phase transition temperatures and the identification of the phases in the embodiments were carried out using DSC measurements and polarized light microscopy. The symbols used here represent the following phases.

Cry: Crystalline phase
Sc*: Chiral smectic C phase
SA: Smectic A phase
Ch: Cholesteric phase
Iso: Isotropic phase

Embodiment 1

/formula/

Manufacture of the 3 – (6 – hexyl – 5, 6 – dihydro – 2H – pyranyl) methyl = 4 – (4 – decyl oxyphenyl) – benzoate) mentioned above.

Process 1

Manufacture of 3 – (2 – cyanoethoxy) nonane nitrile (1).

0.084 g of a 20% potassium hydroxide aqueous solution was added to 1.15 g (0.34 mmol) of 3 – hydroxyl nonane nitrile and 1.23 g (23.2 mmol) of acrylonitrile was instilled for 15 minutes in an ice bath.

When the installation was complete the ice bath was removed and the solution stirred for 24 hours at room temperature. After the reaction was complete, 0.5 ml of 1 M HCl was added and 2 extractions were performed using 20 ml of ether. The ether layer was washed in 20 ML of water and after drying it with anhydrous sodium sulfate, the solvent was removed using vacuum distillation.

(1) This yielded 1.86 G. (8.94 mmol). (Recovery rate: 95.7 %)

bp 130 ° C/0.07 Torr

$[\alpha]_D + 15.6$ $[\alpha]_{435} + 31.1$ (cl, Et₂O)

(Process 2) Manufacture of 3 – (2-methoxy carbonyl ethoxy) methyl nonanoate (2).

0.524 g (2.52 mmol) of the 3 – (2- cyanoethoxy) nonane nitrile (1) produced in process 1 and 0.830 g (25.9 mmol) of dry methanol were placed in a 2-neck, pear shaped flask. 15 ml of concentrated hydrochloric acid were placed in the dropping funnel of the same pressure and 30 ml of concentrated sulfuric acid was placed in a 4-neck flask. After dripping the concentrated hydrochloric acid for 30 minutes, the ice bath was removed. After stirring at room temperature for 19 hours, 0.936 g of water was added, a reflux condenser was attached and the solutions stirred for 22 hours at 50 ° C. After the reaction was finished, water was added until the solids were dissolved. Next, 2 extractions were performed with 10 ml of ether. The ether layer was washed with an aqueous solution of 5 % sodium carbonate. After drying with anhydrous sodium sulfate, the solvent was removed using vacuum distillation. This produced 0.500 g (1.82 mmol) of (2). (Recovery rate: 72.4 %)

bp 100 ° C/0.015 Torr.

$[\alpha]_D - 2.71$ $[\alpha]_{435} - 3.90$ (cl, Et₂O)

(Process 3) Manufacture of 3 – (3-hydroxy propoxy) – 1- nonanol (3).

0.423 g (11.1 mmol) of aluminum lithium hydride and 20 ml of dry ether were placed in a flask. 1.50 g (5.47 mmol) of the 3 – (2-methoxy carbonyl ethoxy) – methyl nonanoate (2) produced in Process 2 in the ice bath was dissolved in 40 ml of dry ether. The solution was then dripped and subjected to heated reflux for 6 hours. After the reaction was finished, 5 ml of water was added to the ice bath. Next, 12 ml of water plus the minimum amount of concentrated hydrochloric acid needed to dissolve the solids that had precipitated were added. Three extractions were run using 10 ml of ether. After drying with anhydrous sodium sulfate, the solution was removed using vacuum distillation.

This produced 1.06 g (4.85 mmol) of (3). (Recovery rate: 88.9 %)

bp 124 ° C/0.030 Torr.

$[\alpha]_D - 18.8$ $[\alpha]_{435} - 35.4$ (cl, Et₂O)

(Process 4) Manufacture of 3 – (2-formyl ethoxy) nonanal (4).

7.08 g (89.6 mmol) of dry pyridine and 100 ml of dry methylene chloride were placed in a flask. This was stirred at room temperature while 4.13 g (41.3 mmol) of chrome trioxide was

added gradually and dissolved. 15 minutes later, 0.746 g (3.42 mmol) of the 3 - (3-hydroxy propoxy) - 1 - nonanol (3) that was produced in Process 3, was dissolved in 5 ml of dry methylene chloride. The solution was then dripped and subsequently mixed for 2 hours at room temperature. After the reaction, the solution was separated using the gradient method, the remainder was washed with ether and placed with the solution. Then it was washed in turns using a 5% sodium hydroxide aqueous solution, 1.5 M hydrochloric acid, a 5% sodium hydroxide aqueous solution and a saturated saline solution. It was then dried with anhydrous magnesium sulfate after which the solvent was removed.

This produced 0.72 g (3.36 mmol) of (3). (Recovery rate: 98.2 %)

(Process 5) Manufacture of 6 - hexyl - 5, 6 - dihydro - 2 H - pyran - 3 carbaldehyde (5).

0.205 g (0.949 mmol) of 3 - (2-formylethoxy) nonanal (4) was dissolved in a 25 ml methanol solution. 0.015 g (0.375 mmol) of sodium hydroxide was dripped into the solution in which 15 ml of methanol had been dissolved and subjected to heated reflux for four hours. After the reaction was finished, 0.1 ml of acetic acid was added and the methanol was removed. 5 ml of ether and 3 ml of water were added and separated. Next, the water layer was extracted twice using 5 ml of ether. The ether layer was washed in an aqueous solution of 5 % sodium carbonate and, after drying with anhydrous sodium sulfate, the solution was removed, yielding 0.181 g (0.923 mmol) mixture of (5) and its isomer 2 - hexyl - 5, 6 - dihydro - 2H - pyran - 3 - carbaldehyde. (Recovery rate: 97.3 %)

(Process 6) Manufacture of 3 - (6-hexyl) - 5, 6 - dihydro -2H - pyranyl methanol (6).

0.060 g (1.58 mmol) of aluminum lithium hydroxide was placed in a reactor container with dry ether and, using ice cooling, a solution containing a 0.218 g (1.11 mmol) mix of the 6 - hexyl - 5, 6 - dihydro - 2 H - pyran - 3 carbaldehyde (5) produced in Process 5 and its isomer 2 - hexyl - 5, 6 - dihydro - 2H - pyran - 3 - carbaldehyde (8b) dissolved in 6 ml of dry ether was dripped before undergoing heated reflux for 4 hours. After the reaction, 10 ml of an ice-cooled, saturated sodium sulfate aqueous solution was added, followed by 10 ml of water and 3 ml of 3 M hydrochloric acid to dissolve the solids. Two extractions were performed using 10 ml of ether. The ether layer was washed with a 5 percent sodium carbonate aqueous solution and dried using anhydrous sodium sulfate. Next the solvent was removed yielding 0.207 g (1.05 mmol) of (6) and its isomer 3 - (2-hexyl) - 5, 6 - dihydro - 2H pyranyl methanol. (Recovery rate: 94.2 %)

(Process 7) Manufacture of Target Chemical Compounds

2 ml of thionyl chloride was added to 0.280 g (0.791 mmol) of 4 - (4 - decyloxyphenyl) benzoate. After 2 hours of heated reflux, the excess thionyl chloride was removed azeotropically. Next, 0.100 g (0.510 mmol) of a benzene solution containing the 3 - (6-hexyl) - 5, 6 - dihydro - 2H - pyranyl methanol (6) that was produced in Process 6 and its isomer 3 - (2-hexyl) - 5, 6 - dihydro - 2H pyranyl methanol and 0.179 g (1.60 mmol) of a benzene solution of triethylene diamine were added. The mixture was stirred for 2 hours at 50 °C and 0.036 g (0.900 mmol) of 60% sodium hydroxide was washed with dry benzene. This was added along with 1 ml of dry benzene and subjected to heated reflux for 2 hours. After the reaction was finished, 3 ml and 5 ml of 1M hydrochloric acid were added and, after filtering out the solids, 2 extractions were performed using 10 ml of benzene. The benzene layer was washed using anhydrous sodium sulfate and, after removing the solvent, it was purified using thin-layer chromatography. (After separation using a ratio of expansion solvent/hexane to methylene chloride of 1 to 5, it was expanded 20 times using a hexane-to-benzene ratio of 1 to 1.)

It was recrystallized using hexane. 0.028 g (0.0526 mmol) of the target chemical compound was produced. (Recovery rate: 9.7%)

$[\alpha]_D - 25.2$ $[\alpha]_{435} - 42.0$
(c0.26, CHCl₃)
¹H – NMR δ [ppm]
0.87 (6H, m), 1.2 – 2.2 (28H, m)
3.46 (1H, m), 3.99 (2 H, t),
4.29 (2H, m), 4.73 (1H, s)
5.96 (1H, m), 6.97 (2H, d),
7.54 (2H, d), 7.60 (2H, d),
8.06 (2H, d)

Phase Transition Temperature (°C); DSC, Polarized Microscope

Cry 94 Iso
 88

Embodiment 2

The optically-active chemical compound described in Embodiment 1 was used as an ingredient in preparing the liquid crystal compositions A and B described below.

| | Liquid Crystal Composition A | Liquid Crystal Composition B |
|-----------------------------------|------------------------------|------------------------------|
| /formula/ Amounts Added (wt %) | 5.0 | 19.9 |
| /formula/ Amounts Added (wt %) | 95.0 | 80.1 |

Transition Temperature of the Liquid Crystal Composition A (°C)

DSC, Polarized Microscope

/formula/

Transition Temperature of the Liquid Crystal Composition B (°C)

DSC, Polarized Microscope

/formula/

Embodiment 3

The optically-active chemical compound described in Embodiment 1 was used as an ingredient in preparing liquid crystal composition C described below.

| | Liquid Crystal Composition C |
|-----------------------------------|------------------------------|
| /formula/ Amounts Added (wt %) | 8.2 |
| /formula/ Amounts Added (wt %) | 7.5 |
| /formula/ Amounts Added (wt %) | 84.3 |

Transition Temperature of the Liquid Crystal Composition A (°C)

DSC, Polarized Microscope

/formula/

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